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Journal of the European Ceramic Society 27 (2007) 3105–3108

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Microwave dielectric properties of porous Mg_2SiO_4 filling with TiO_2 prepared by a liquid phase deposition process

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Abstract

Forsterite (Mg_2SiO_4) possesses a high quality factor ($Q{\cdot}f$) of 270,000 GHz and a low dielectric constant ε_r of 6.8. However, it shows a relatively large negative temperature coefficient of resonant frequency τ_f of −73 ppm/°C. For microwave telecommunication, a τ_f of nearly 0 ppm/°C is desirable to keep the frequency stability. In order to improve τ_f, we have tried to produce pure Mg_2SiO_4–TiO_2 composite ceramics with no secondary phases using a liquid phase deposition (LPD) method. Porous Mg_2SiO_4 ceramics was prepared by sintering Mg_2SiO_4 with polymethyl methacrylate (PMMA) particles, and then TiO_2 was filled in the pores of Mg_2SiO_4 by the LPD method. The porosity and microstructure of porous Mg_2SiO_4 was controlled by amount and particle sizes of PMMA and formation process. τ_f of Mg_2SiO_4 filled with TiO_2 by LPD method was improved to −46 ppm/°C.

Keywords: Dielectric properties; Mg_2SiO_4

1. Introduction

Recent developments in microelectronics technologies have created a great demand for microwave substrate materials with a very low dielectric constant (ε_r) to reduce the delay time of electronic signal, a very high quality factor ($Q{\cdot}f$) to achieve high selectivity and nearly zero temperature coefficient of resonant frequency (τ_f) for frequency stability. Forsterite (Mg_2SiO_4) is a candidate for the microwave substrate. However, it has large negative τ_f (−70 ppm/°C). In order to adjust the τ_f value near to zero, TiO_2 with high positive τ_f value (450 ppm/°C) was added to the Mg_2SiO_4. In the previous paper, one of the authors has reported that Mg_2SiO_4–TiO_2 composite ceramics prepared by ordinary solid state reaction was improved τ_f to 0 ppm/°C.[1,2] However, $Q{\cdot}f$ of the composite ceramics decreased because of other phases such as $MgTi_2O_5$ and $MgSiO_3$ caused by a chemical reaction between Mg_2SiO_4 and TiO_2 during sintering. The present study was conducted to produce pure Mg_2SiO_4–TiO_2 composite ceramics with no secondary phases using a liquid phase deposition (LPD) method. Porous Mg_2SiO_4 ceramics was prepared by sintering Mg_2SiO_4 with polymethyl methacrylate (PMMA) particles as pore forming agent, and then TiO_2 was filled in the pores of Mg_2SiO_4 by the LPD method.

2. Experimental procedures

2.1. Porous Mg_2SiO_4 ceramics

High purity chemicals such as $Mg(OH)_2$ (99.98%) and SiO_4 (99.9%) powders were weighed in stoichiometric ratios and mixed and ball-milled for 24 h using zirconia balls as the grinding media and ethanol as the solvent. After drying, the powder was calcined at 1150 °C for 2 h in air. Two types of PMMA powders with an average particle size of 5.0 and 1.5 μm were used as pore-forming agent. The calcined powder and xPMMA, where $x = 0$, 10, 30 and 50 vol%, respectively, was ball-milled again for 24 h and dried. The powder was prepared in two ways: firstly it was pressed into only cylindrical shape under a uniaxial pressure of 7.84 MPa and secondly subsequent to the first step they were then pressed by cold isostatic press (CIP) up to 200 MPa. These pellets were then sintered in air at 1400 °C for 2 h. Sintered discs were polished and annealed in air at 1000 °C for 2 h.

The bulk densities of sintered samples were measured by the Archimedes method using distilled water. The microstructure of the samples was observed by a scanning electron microscope (SEM).

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doi:10.1016/j.jeurceramsoc.2006.11.032

2.2. Liquid phase deposition process

Ammonium hexafluorotitanate [$(NH_4)_2TiF_6$] and boric acid (H_3BO_3) were dissolved in distilled water. These solutions were mixed and used as treatment solutions. The resultant concentration was 0.1 mol/l for $(NH_4)_2TiF_6$ and 0.2 mol/l for H_3BO_3.[3,4] The porous Mg_2SiO_4 ceramics was immersed in the treatment solution and then evacuated for 1 h and maintained for 24 h. Anatase TiO_2 was deposited on the surface of the sample. It was then washed with distilled water and annealed at 700 °C.

The microwave dielectric properties were measured by the Hakki and Coleman resonator method,[5] where a cylindrically shaped specimen is positioned between two copper plates. A network analyzer (Agilent 8720ES) was used as the measuring system. The dielectric constant was calculated by the resonant frequency of the TE_{011} resonant mode. The temperature coefficient of the resonator frequency was obtained in the temperature range from 20 to 80 °C.

3. Results and discussion

3.1. Porous Mg_2SiO_4 ceramics

The porosity varied with the volume fraction of PMMA as shown in Fig. 1. It is found that the porosity monotonously increased with increasing PMMA content. As compared with particle size of PMMA, the porosity of the samples with 5.0 μm PMMA particles was higher than that of 1.5 μm PMMA particles although the same volume of PMMA was added. Particle size of calcined Mg_2SiO_4 powder was about 1–3 μm. In the case of 5.0 μm PMMA, it is assumed that during the sintering process the pores are prevented from contraction because their size was larger compared with Mg_2SiO_4 powder. The porosity of the samples with 1.5 μm PMMA without CIP process was higher than used by CIP process, particularly a significant difference can be seen in the samples with 50 vol% PMMA. It can be interpreted that in the samples without CIP process, Mg_2SiO_4 particles do not have many contacts to other particles and thus no sintering process take place.

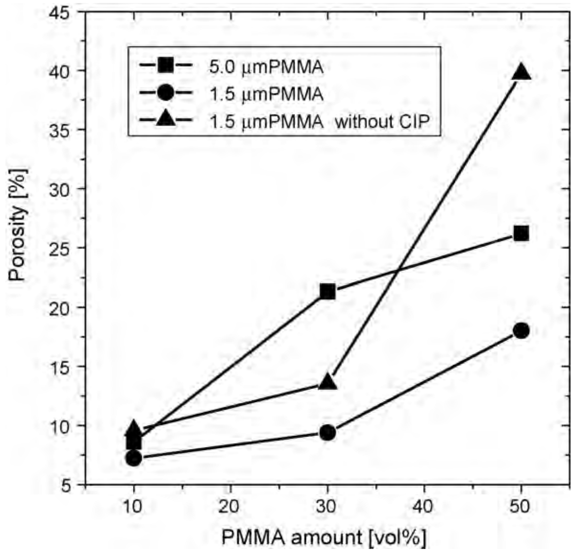

Fig. 1. Variation of porosity by volume fraction of PMMA.

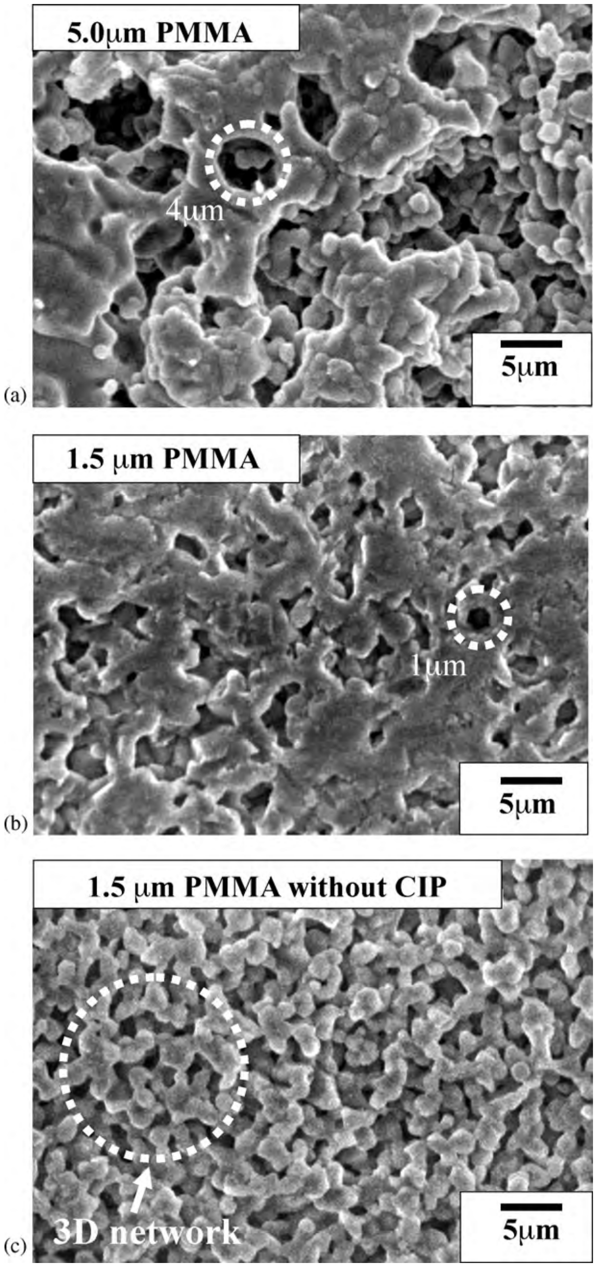

Fig. 2. SEM images showing the surface appearances of porous Mg_2SiO_4 ceramics sintered with amount of 50 vol% PMMA.

Fig. 2(a–c) shows the SEM images of the samples sintered with 50 vol% PMMA. Microstructures with various pore sizes were observed. It is found that the pore size becomes smaller as the particle size of PMMA decreased. In Fig. 2(c) many open-pore and 3D network was observed in the sample doped 50 vol% PMMA content without CIP process. This suggests that the content and particle size of doped PMMA as well as use or not of CIP can control the porosity and microstructure of the Mg_2SiO_4 ceramics.

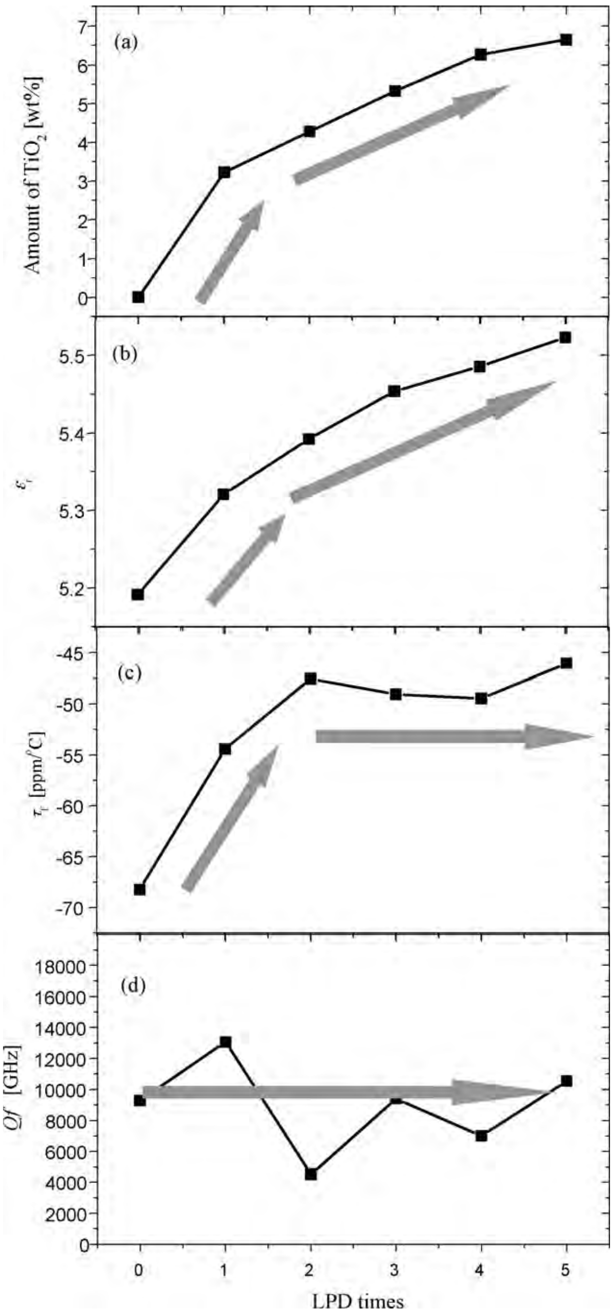

Fig. 3. Variations of (a) amount of deposited TiO_2, (b) dielectric constant ε_r and (c) temperature coefficient of resonant frequency τ_f (d) quality factor $Q\cdot f$ as a function of LPD times.

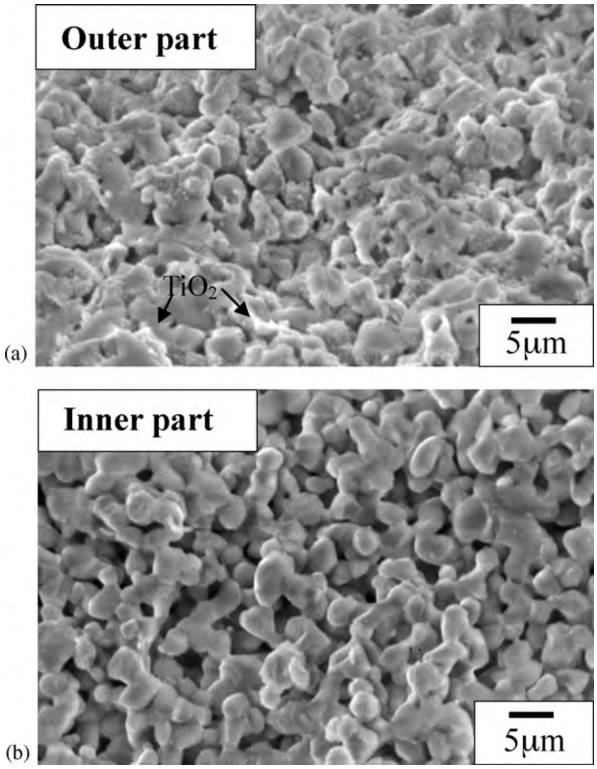

Fig. 4. SEM images of the section of porous Mg_2SiO_4 ceramics filled with TiO_2 by five times LPD; (a) outer part and (b) inner part.

3.2. Filling with TiO_2 by LPD method

In this study, LPD process was practiced with the porous Mg_2SiO_4 sample, where the porosity is about 40%. The sample was prepared by mixing 50 vol% 1.5 μm PMMA and then pressing without CIP process. Fig. 3(a–d) shows the effect of LPD times on the amount of TiO_2 and dielectric properties. In Fig. 3(a) it is seem that TiO_2 weight increased with increasing number of LPD times. After first LPD, the increase of TiO_2 weight becomes slow. It is considered that deposited TiO_2 on the surface of the Mg_2SiO_4 sample prevent an invasion of the treatment solution. As shown in Fig. 3(b), ε_r value increases with increasing number of LPD times and the increase is similar to the variation of TiO_2 weight% with LPD times. τ_f value was improved from −68 to −46 ppm/°C by filling TiO_2 in pores of Mg_2SiO_4 by the LPD method. After two times LPD, however, τ_f value of the sample was not improved although the amount of deposited TiO_2 increased. This result suggests that the amount of TiO_2 filled in porous Mg_2SiO_4 is a little or the TiO_2 reacts with Mg_2SiO_4 during annealing treatment. The samples filled with TiO_2 has low $Q\cdot f$ value about 10,000 GHz. In other words, filling the open porosity do not improve $Q\cdot f$ value. In this case, one needs to consider the amount of porosity Mg_2SiO_4 samples and the amount of deposited TiO_2. SEM images in Fig. 4(a and b) shows the comparison of the sectioned porous Mg_2SiO_4 ceramics filled with TiO_2 by five times by LPD method. It is seen that in the inner part a few pores were filled with TiO_2 compared with the outer one. Further work is needed to understand the effect of the concentration of LPD treatment solution and annealing temperature on construction of the pore filling.

4. Conclusions

In this study, for the purpose of improving τ_f value, porous Mg_2SiO_4 ceramics was prepared by sintering Mg_2SiO_4 with PMMA particles as pore forming agent, and then TiO_2 was filled in the pores of Mg_2SiO_4 by the LPD method. Porosity and microstructure of porous Mg_2SiO_4 ceramics was controlled by amount and particle size of PMMA and formation process. A small amount of TiO_2 which is about 6.5 wt% has been filled using LPD method. τ_f value was improved from -68 to -46 ppm/°C by filling TiO_2 with several times LPD process. Further studies are needed to understand the effect of the concentration of treatment solution of LPD and annealing temperature on construction of the pore filling.

Acknowledgement

A part of this study was supported by a Grant-in Aid for Scientific Research (B) from Japanese Ministry of Education, Science and Culture.

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